June 14, 2002

AAD Document Control
U.S. Department of Energy
National Energy Technology Laboratory
626 Cochrans Mill Road, MS 921-107
Pittsburgh, PA 15236-0940

Dear AAD Document Control:

Subject: Final Report for Joint Venture Task 37 – Evaluation of SO_3 Emission Control by Flue
Gas Humidification at the R. Paul Smith Station; Cooperative Agreement No.
DE-FC26-98FT40321; UND Fund 4431

Please find enclosed one copy and an electronic version of the final report mentioned
above. The draft copy was sent to the performance monitor on April 8, 2002, for her review. The
changes were incorporated. Also enclosed is the Patent Clearance Form.

If you have any questions, please feel free to contact me by telephone at (701) 777-5124,
by fax at (701) 777- 5181, or by e-mail at slandis@undeerc.org.

Sincerely,

Sheryl E. Landis
Manager, Contracts and Intellectual Property
Business and Operations

DLL/tab

Enclosure

c/enc: Richard Read, NETL
Greg Weber, EERC
Stan Miller, EERC

June 14, 2002

Dr. Bernie Hamel
Marsulex Environmental Technologies LLC
200 North 7th Street
Lebanon, PA 17046

Dear Dr. Hamel:

Subject: Final Report for Joint Venture Task 37 – Evaluation of SO_3 Emission Control by Flue
Gas Humidification at the R. Paul Smith Station; Cooperative Agreement No.
DE-FC26-98FT40321; UND Fund 4431

Please find enclosed the U.S. Department of Energy (DOE) final report for the above
agreement. At the request of the DOE Performance Monitor, Susan Maley, some minor changes
have been made to the report to add more explanation as to why variations in data occurred.
Therefore, we thought you might like to have a copy of the revised report.

If you have any questions, please feel free to contact me by telephone at (701) 777-5138,
by fax at (701) 777-5181, or by e-mail at dlaudal@undeerc.org.

Sincerely,

Dennis L. Laudal
Senior Research Advisor

DLL/tab

Enclosure

c/enc: Susan Maley, NETL
        Michael Jones, EERC

c: Richard Read, NETL
    Greg Weber, EERC

U.S. DEPARTMENT OF ENERGY
National Energy Technology Laboratory

REQUEST FOR PATENT CLEARANCE FOR
RELEASE OF CONTRACTED RESEARCH DOCUMENTS

TO:

■ For Technical Reports
  AAD Document Control
  U.S. Department of Energy - NETL
  MS 921-107
  P.O. Box 10940
  Pittsburgh, PA 15236-0940

□ For Technical Papers/Journal Articles/Presentations
  Mark P. Dvorscak
  U.S. Department of Energy
  9800 S. Cass Avenue
  Argonne, IL 60439
  FAX: (630) 252-2779

♦ **Cooperative Agreement No.**
DE-FC26-98FT40321

Name & Phone No. of DOE COR
Dr. Richard Read
(412) 386-5721

A. CONTRACTOR ACTION (CONTRACTOR COMPLETES PART A. 1-5)

1. Document Title: Final Report for JV Task 37 – Evaluation of SO_3 Emission Control by Flue Gas Humidification at the R. Paul Smith Station.

2. Type of Document: □ Quarterly Status Report   □ Topical Report   ■ Final Technical Report
   □   Abstract   □   Technical Paper   □   Journal Article   □ Conference Presentation
   □   Other (please specify):

3. Date clearance needed:

♦4. Patent information
  Yes   No
   □   ■   Is any patentable subject matter disclosed in the report?
   □   □   If so, has an invention disclosure been submitted to DOE Patent Counsel?
             If yes, identify disclosure number or DOE Case Number
   □   ■   Are there any patent-related objections to the release of this report? If so, state the objections.

♦ 5. Signed _____   Date _____
                          (Contractor)
Name & Phone No.   Sheryl E. Landis, (701) 777-5124
Address   University of North Dakota, PO Box 9018, Grand Forks, ND 58202

B. DOE PATENT COUNSEL ACTION

   □   Patent clearance for release of the above-identified document is granted.
   □   Other : _____
Signed _____   Date _____
             (Patent Attorney)

♦ Must be completed by the contractor.

EVALUATION OF SO₃ EMISSION CONTROL BY FLUE GAS HUMIDIFICATION AT THE R. PAUL SMITH STATION

Final Report

For the period April 23, 2001, through June 30, 2002

Prepared for:

AAD Document Control
U.S. Department of Energy
National Energy Technology Laboratory
PO Box 10940, MS 921-107
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Prepared by:

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2002-EERC-06-04   June 2002

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURE

EERC   Energy & Environmental Research Center
EPA   U.S. Environmental Protection Agency
ESP   electrostatic precipitator
FGD   flue gas desulfurization
MET   Marsulex Environmental Technologies LLC
NO_x nitrogen oxides
SCR   selective catalytic reduction
SO_3 sulfur trioxide
XRF   x-ray fluorescence

EVALUATION OF SO$_3$ EMISSION CONTROL BY FLUE GAS HUMIDIFICATION AT THE R. PAUL SMITH STATION

EXECUTIVE SUMMARY

Introduction

Depending on the size and type of boiler, the 1990 Clean Air Act Amendments required specific reductions in SO$_2$ and NO$_x$ emissions from coal-fired electric utilities. To meet these requirements, SO$_2$ reduction strategies have included installing scrubbing technology, switching to a more expensive low-sulfur coal, or purchasing SO$_2$ allowances. It is expected that over the next 10 years there will be an increase in the price of low-sulfur coals, but that higher-sulfur coal costs will remain the same. Technologies must be strongly considered that allow the use of high-sulfur fuels while at the same time meeting current and future SO$_2$ emission limits. In addition, it is expected that many new selective catalytic reduction (SCR) systems will be installed to reduce NO$_x$.

A point of concern for flue gas desulfurization (FGD) and SCR systems is the emission of sulfuric acid/sulfur trioxide (SO$_3$) aerosols that could result in increased opacity at the stack as a direct result of firing high-sulfur fuels that naturally generate more SO$_3$ than do low-sulfur coals. SO$_3$ is formed during the coal combustion process and converted to gaseous (H$_2$SO$_4$) by homogeneous condensation, leading to a submicron acid fume that is very difficult to capture in a dry electrostatic precipitator (ESP). Also, the condensed acid can combine with the fly ash in the duct and scale the duct wall, potentially resulting in problems.

EPRI conducted a bench-scale experimental study to test the effect of flue gas humidification on SO$_3$ emission control in the 1980s. Later, two demonstration test programs were conducted: one in the early 1990s at EPRI's high-sulfur test center and the other in the mid-1990s by the Tennessee Valley Authority at a 10-MW facility. The results from these tests showed decreased SO$_3$ emissions at lower flue gas temperatures, typically in the range of 250° to 280°F (121° to 138°C). It was concluded that the SO$_3$ selectively condenses on the available fly ash and is then neutralized by the inherent alkalinity of the fly ash.

Thus the Energy & Environmental Research Center (EERC) was contracted by Marsulex Environmental Technologies LLC (MET) and the U.S. Department of Energy to evaluate potential for reducing SO$_3$ emissions at the R. Paul Smith Station by lowering the flue gas temperature with humidification.

Approach

To evaluate the use of humidification to reduce SO$_3$ emissions at the full-scale level, Unit 4 at the R. Paul Smith Station was selected. It has an existing flue gas humidification system, with adjustable water injection rates of 0 to 12 gal/min (45.4 L/min). Three locations were selected for sampling: the air heater inlet, the ESP inlet, and the stack. At each sample point, the particulate mass loading and gas-phase SO$_3$ were measured. By injecting additional

SO$_3$ gas into the duct upstream of the air heater, the SO$_3$ concentration in the flue gas at the injection location was varied from 10 to 50 ppmv. A summary of the test matrix is given in Table ES-1.

Table ES-1. Tests Conducted at the R. Paul Smith Station

SO$_3$ Conc., ppmv	Water Injection Rate, gal/min				
	0	6	8	9	12
0	✔				
10	✔		✔		✔
30	✔	✔		✔	✔
50	✔	✔		✔	✔

Results

Extensive SO$_3$ sampling tests were carried out by the EERC and MET at the R. Paul Smith Station in Maryland. The purpose of the tests was to demonstrate the potential of flue gas humidification to reduce SO$_3$ emissions even at relatively high concentrations of SO$_3$. The coal fired by the R. Paul Smith Station was a low-sulfur Maryland eastern bituminous coal.

Following a baseline test (no SO$_3$ injection), tests were conducted with various concentrations of SO$_3$ injected approximately 30 feet (9.1 m) upstream of the air heater (Table ES-1). For all tests, the vapor-phase SO$_3$ was sampled at the air heater inlet, the ESP inlet, and the stack simultaneously. The resulting vapor-phase SO$_3$ concentrations and the total removal efficiency are plotted in Figure ES-1 as a function of sampling location and different SO$_3$ injection levels. As expected, the stack vapor-phase SO$_3$ emissions increased as the injection level increased. The stack vapor-phase SO$_3$ emissions were 8.1 and 13.2 ppmv for the SO$_3$ injection levels of 30 and 50 ppmv, respectively. In general, the data showed an inverse correlation between the collection efficiency and initial SO$_3$ vapor concentration, which is in agreement with the theoretical analysis.

The fly ash collected from the U.S. Environmental Protection Agency Method 5 filter at the three sampling locations was analyzed for sulfates (all sulfate concentrations were converted to SO$_3$ concentrations). With increasing SO$_3$ injection rates from 0 to 50 ppmv, the sulfate concentration on the fly ash collected at the air heater increased from 1780 ppmv for the baseline condition up to 6180 ppmv when 50 ppmv was injected. These results indicate that the SO$_3$ vapor was transferred to the particulate phase during condensation. It appears that most of the depleted SO$_3$ vapor is condensed in the air heater. The sulfate was clearly enriched on the fine fly ash emitted at the stack as a result of condensation of SO$_3$ vapor on fly ash particles and the formation of sulfuric acid mist. The higher sulfate concentration on the fine fly ash at the stack when 50 ppmv SO$_3$ was injected compared to the 10-ppmv injection test indicated that more fine sulfate aerosols were formed in the ESP at the higher SO$_3$ concentration. Not surprisingly, the
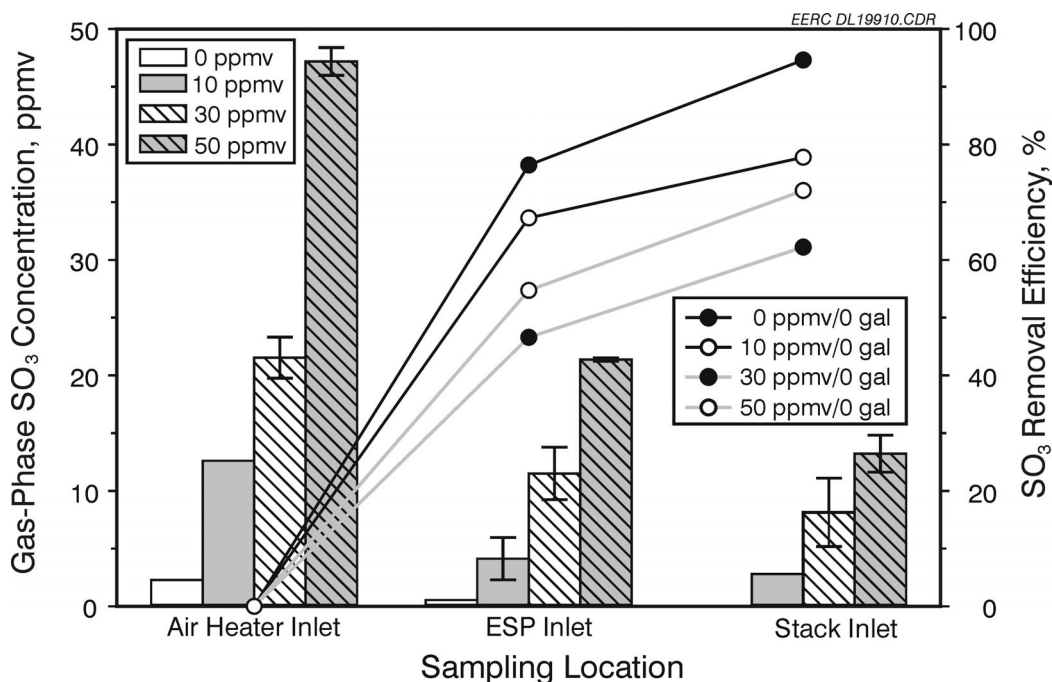
Figure ES-1. SO$_3$ concentration and removal efficiency with no humidification.

total sulfur concentrations in the fly ash were approximately the same as the sulfate concentration, showing most of the sulfur species were in the sulfate form.

Tests were then conducted using flue gas humidification. Humidification of the flue gas enhances SO$_3$ condensation by decreasing flue gas temperature. Once the SO$_3$ has condensed, the ESP removes it from the flue gas. In addition, ESP performance is generally enhanced because of reduced flue gas temperature and the presence of SO$_3$. By reducing the temperature and adding SO$_3$, the ash resistivity is reduced. SO$_3$ samples were collected and analyzed at different humidification and SO$_3$ injection levels at the air heater inlet, ESP inlet, and stack. The results of the humidification tests at various SO$_3$ injection levels are shown in Table ES-2. The results show the benefit of using humidification. The overall SO$_3$ removal was >90% at a humidification level of 12 gal/min (45.4 L/min) for all SO$_3$ concentrations tested. In general, the SO$_3$ collection efficiency appears to be relatively linear, as shown by the regression line in Figure ES-2.

Conclusions

The conclusions for the sampling at the R. Paul Smith Station to determine the effect of humidification on SO$_3$ emissions are as follows:

- The fly ash was able to remove SO$_3$ efficiently at the baseline conditions (no SO$_3$ injection or humidification).

- SO$_3$ emissions were significantly reduced with flue gas humidification.

Table ES-2. The Effect of Humidification on Vapor-Phase SO$_3$

Humid. Level:	0 gal/min	6 gal/min		8 gal/min		9 gal/min		12 gal/min	
Nominal SO$_3$ Injection, ppm	Total Vapor-Phase SO$_3$ Removal,[a] %	Total Vapor-Phase SO$_3$ Removal,[a] %	Additional SO$_3$ Removal Because of Humid.,[b] %	Total Vapor-Phase SO$_3$ Removal,[a] %	Additional SO$_3$ Removal Because of Humid.,[b] %	Total Vapor-Phase SO$_3$ Removal,[a] %	Additional SO$_3$ Removal Because of Humid.,[b] %	Total Vapor-Phase SO$_3$ Removal,[a] %	Additional SO$_3$ Removal Because of Humid.,[b] %
0	94.6								
10	77.8			87.5	17.8			90.9	18.3
30	62.2	71.4	0.7			88.3	14.0	92.4	20.5
50	72.2	78.8	7.6			75.6	13.3	90.3	21.9

[a] Calculated based on the air heater inlet SO$_3$ concentration compared to the stack SO$_3$ concentration.
[b] Calculated by subtracting the total SO$_3$ removal with no humidification from that calculated at the various humidification levels. To put all tests on the same basis, the average air heater inlet SO$_3$ concentration (45.3 ppmv) was used (the air heater inlet value at 9 gal/min is assumed to be a bad measurement and was ignored).
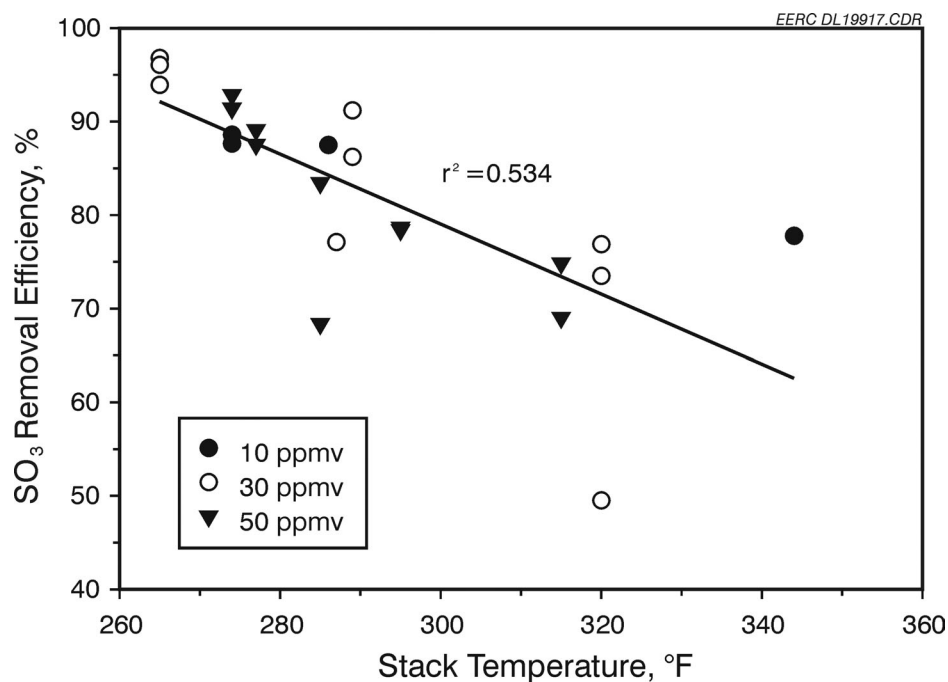
Figure ES-2. Overall SO_3 removal efficiency as a function of stack temperature.

- The highest SO_3 collection efficiency, 96.8%, was achieved at a flue gas temperature of 265°F (129°C).

EVALUATION OF SO$_3$ EMISSION CONTROL BY FLUE GAS HUMIDIFICATION AT THE R. PAUL SMITH STATION

1.0   INTRODUCTION

Depending on the size and type of boiler, the 1990 Clean Air Act Amendments required specific reductions in SO$_2$ and NO$_x$ emissions from coal-fired electric utilities. To meet these requirements, SO$_2$ reduction strategies have included installing scrubbing technology, switching to a more expensive low-sulfur coal, or purchasing SO$_2$ allowances. It is expected that over the next 10 years there will be an increase in the price of low-sulfur coals, but that higher-sulfur coal costs will remain the same. As a result, many utilities will be installing both conventional and more novel flue gas desulfurization (FGD) systems to allow the use of higher-sulfur coal and at the same time meet more stringent SO$_2$ emission levels.

The most common NO$_x$ reduction strategy is the installation of low-NO$_x$ burners. These burners have the capability of reducing NO$_x$ emissions by 40%–60%. However, with possible establishment of PM$_{2.5}$, regional haze, and ozone regulations, there is increased incentive to reduce NO$_x$ emissions to a level below what can be achieved using low-NO$_x$ burners. Selective catalytic reduction (SCR) technology, which can reduce NO$_x$ emissions by >90%, is, therefore, becoming more attractive, particularly because catalyst costs continue to decrease and the knowledge base for using SCR reactors is expanding. Within the next 5 years, 80 to 90 U.S. utilities are planning to install SCR units (1).

A point of concern for FGD and SCR systems is the emission of sulfuric acid/sulfur trioxide (SO$_3$) aerosols. SO$_3$ is formed during the coal combustion process and converted to gaseous H$_2$SO$_4$ by homogeneous condensation, leading to a submicron acid fume that is very difficult to capture in a dry electrostatic precipitator (ESP). This could result in increased opacity at the stack. The potential for increased SO$_3$ aerosol emissions is a direct result of firing high-sulfur fuels that naturally generate more SO$_3$ than do low-sulfur coals. Also, with the expected increased used of SCR technology, potentially a higher percentage of SO$_2$ may be converted to SO$_3$.

In the 1980s, EPRI conducted a bench-scale experimental study to test the effect of flue gas humidification on SO$_3$ emission control (2). Later, two demonstration test programs were conducted, one in the early 1990s at EPRI's high-sulfur test center and the other in the mid-1990s by the Tennessee Valley Authority at a 10-MW facility (3, 4). The results from these tests showed decreased SO$_3$ emissions at lower flue gas temperatures, typically in the range of 250° to 280°F. It was concluded that the SO$_3$ selectively condenses on the available fly ash and is then neutralized by the inherent alkalinity of the fly ash.

Thus the Energy & Environmental Research Center (EERC) was contracted by Marsulex Environmental Technologies LLC (MET) and the U.S. Department of Energy to evaluate the potential for reducing SO$_3$ emissions at the R. Paul Smith Station by lowering the flue gas temperature with humidification.

2.0 PROJECT GOALS AND OBJECTIVES

The overall goal of the project was to demonstrate at the full-scale level the reduction in SO_3 emissions that occurs as a result of flue gas humidification, even at relatively high concentrations of SO_3. A specific objective was to inject relatively high levels of SO_3 into the flue gas stream without negatively impacting stack opacity.

3.0 TEST FACILITIES

3.1 R. Paul Smith Station

The R. Paul Smith Station is owned and operated by the Potomac Edison Company and Allegheny Power. The tests were conducted on Unit 4, which has an 87-MW capacity. The coal fired is a Maryland bituminous coal. The unit is a pulverized coal, tangentially fired boiler equipped with low-NO_x burners. Unit 4 has a cold-side ESP for particulate control but has no FGD system. To improve the performance of the ESP, Unit 4 is equipped with a humidification system that is designed to cool the flue gas from 300°F (149°C) to 265°–270°F (129°–132°C).

3.2 SO₃ Injection Systems

The field sampling activities at the R. Paul Smith Station required the addition of SO_3 to the flue gas. An SO_3 injection skid manufactured by Wahlco, Inc., was used. The Wahlco skid-mounted system generated SO_3 by converting anhydrous SO_2 to SO_3. The anhydrous SO_2 was delivered at a minimum of 40 psig (377.11 kPa) to a heater vessel where it was mixed with air and heated to about 800°F (427°C) above ambient. A blower was used to deliver the process air, rated at 350 cfm (0.165 m^3/s) at 2 psi (13.79 kPa), to the unit. The heating vessel contained six tubular heaters, each rated at 16 kW. Once heated, the SO_2 passed to the unit through the converter vessel containing a vanadium/titanium catalyst. The catalyst had a conversion efficiency of about 95%. Controlling the converter inlet temperature and the SO_2 flow rate to the catalyst regulated the amount of generated SO_3. The converter vessel was designed to convert a maximum of 170 lb/hr (21.42 kg/s) of SO_2, resulting in a rate of 20 to 200 lb/hr (2.52 to 25.2 kg/s) of SO_3.

4.0 MEASUREMENT AND SAMPLING PROCEDURES FOR SO₃

4.1 SO₃ Measurement

For SO_3 measurements, the controlled condensation technique was used. This method uses a water bath to control the temperature in a condenser at 142°F (61°C). At this temperature, the SO_3 condenses and is retained on a glass wool plug and on the inside of the condenser. The SO_2 and water vapor continue on through the condenser in the gaseous state. Once the gas has passed through the condenser, it is passed through two impingers containing a hydrogen peroxide solution in which the SO_2 is absorbed. A schematic of the selective condensation system is shown in Figure 1. Sampling data, recorded at a regular interval during the tests, included probe
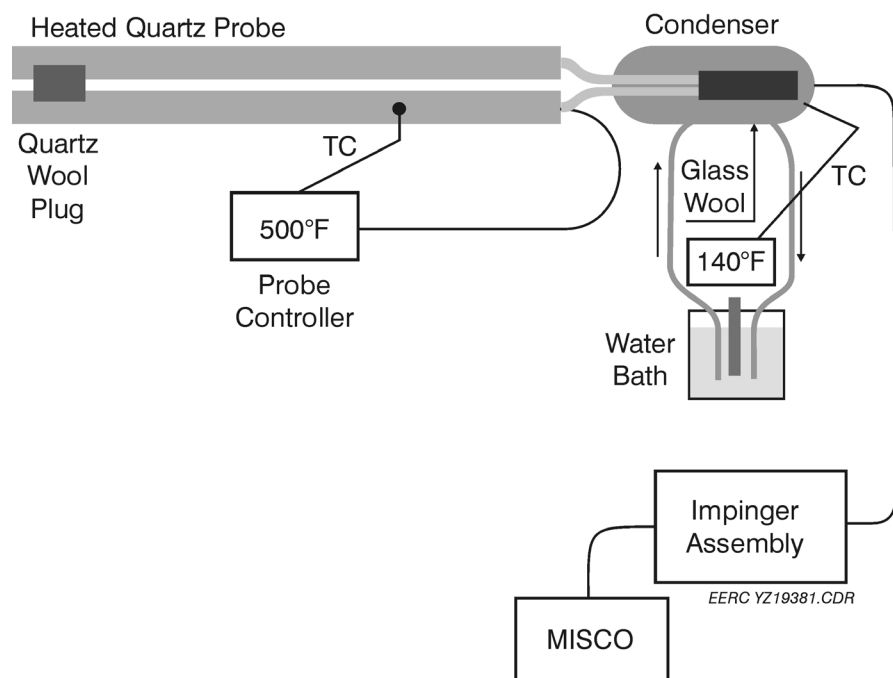
Figure 1. Schematic of the selective condensation system for measuring gas-phase SO_3.

temperature, condenser temperature, stack temperature, flowmeter readings, gas meter temperatures, system pressures, barometric pressure, and sampling time period. After completing the sampling, a leak check was carried out for the probe, and the condenser was rinsed using deionized water to recover the condensed SO_3 for analysis by ion chromatography.

Particulate SO_3 (as SO_3 aerosols and SO_4^{-2}) was sampled using the conventional bulk sampling procedures as defined by U.S. Environmental Protection Agency (EPA) Method 5/17. This method provided the total particulate mass loading. The filters were then digested in acid bomb and the resulting solution analyzed using ion chromatography for total SO_4^{-2}.

4.2   Mercury

Although mercury concentration was not a major component of the overall project, it was measured in both the flue gas and fly ash. The method used to measure mercury in the flue gas was the Ontario Hydro (OH) mercury speciation method. This method is a modification of EPA Method 5/17 where a series of impingers are used to separate the species of mercury in the flue gas (elemental mercury and oxidized mercury). The impinger solutions are then analyzed using cold-vapor atomic adsorption techniques. A detailed description of the method is provided at the following Web site: http//www.epa.gov/ttn/emc/prelim.html.

4.3   Coal and Fly Ash

The following analyses were performed on the composite fuel samples and the fly ash collected from the ESP hoppers. Most of the methods used for these measurements are standard techniques as defined by the American Society for Testing and Materials or EPA.

Fly Ash

- Loss on ignition
- Carbon content (carbon, hydrogen, nitrogen analysis)
- X-ray fluorescence (XRF) (major elements and some trace elements)

Fuel

- Mercury
- Chlorides
- Ultimate–proximate
- Btu
- XRF (major and some trace elements)

5.0   TECHNICAL APPROACH

Unit 4 at R. Paul Smith Station was selected for testing because it already had an existing flue gas humidification system. The humidification system, located upstream of the ESP, had an adjustable water injection rate of 0 to 12 gal/min (45.4 L/min). For this project, a commercial SO_3 generator (discussed previously in Section 3.2) was used to catalytically convert anhydrous SO_2 to SO_3. The SO_2–air mixture (controlled at 750°–850°F [399°–454°C]) passed into the converter to be oxidized to SO_3 with a designed efficiency of about 95%.

The SO_3 system was calibrated by the supplier and sized to provide an SO_3 concentration in flue gas in the range of 10 to 50 ppmv. The SO_3 lances for the injection system were installed into the duct at a location approximately 30 feet (9.1 m) upstream of the air heater.

Three locations were selected for sampling: the air heater inlet, the ESP inlet, and the stack. A schematic showing the sampling locations is presented in Figure 2. At each location, EPA Method 5 was used to collect particulate samples to determine total particulate mass loading. In addition, the particulate matter collected on the filter was analyzed to measure the sulfate concentration. Although not exact because of fly ash SO_2 reactions, this allowed a reasonable approximation of the fraction of SO_3 in the solid phase. The gas-phase SO_3 was measured using the controlled condensation method. This method was discussed in Section 4.2. In this way, the variation of SO_3 through the system could be determined, giving some insight into the potential collection of SO_3 in various components of the system.

By injecting additional SO_3 gas into the duct, the SO_3 concentration in the flue gas at the injection location was varied from 10 to 50 ppmv. The water injection rate was also adjusted
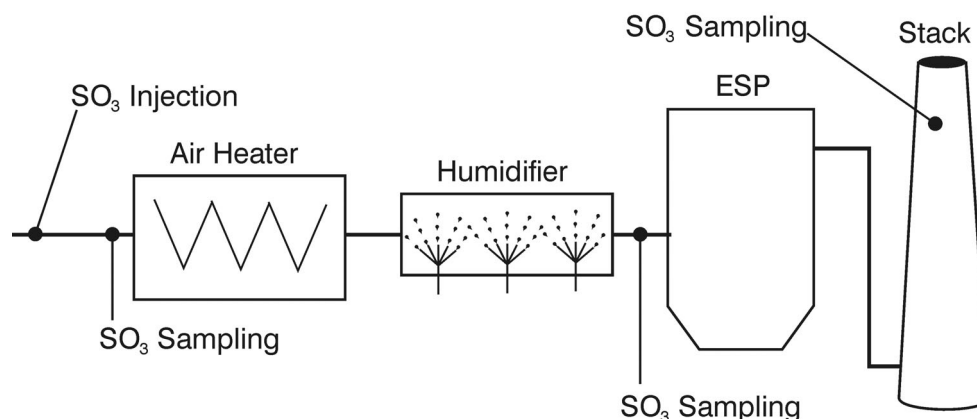
Figure 2. Schematic showing the sampling locations at the R. Paul Smith Station.

from 0 to 12 gal/min (0–45.4 L/min) to reduce the flue gas temperature. SO_3 samples were collected at the three sampling locations simultaneously under the different operating conditions. A summary of the test matrix is given in Table 1. Test 1 was conducted as a baseline to examine the effectiveness of the fly ash without humidification on SO_3 removal. Tests 2–5 were performed to evaluate the effect of various levels of humidification on SO_3 emission control. For each test, two controlled condensation and two EPA Method 5 sampling procedures were performed at each of the three sample points. Sampling was started approximately 1 hour after the SO_3 injection rate was changed to ensure stable operating conditions.

Table 1. Tests Conducted at the R. Paul Smith Station

SO_3 Conc., ppmv	Water Injection Rate, gal/min				
	0	6	8	9	12
0	✔				
10	✔		✔		✔
30	✔	✔		✔	✔
50	✔	✔		✔	✔

Although not a primary focus of the testing, mercury concentrations were measured at the ESP inlet and the stack for several of the test conditions using the OH mercury speciation method. The purpose was to examine the effects of humidification and SO_3 concentration on mercury speciation. For documentation purposes and to put the analyses on a consistent basis, the plant also monitored the O_2, CO_2, CO, NO_x, and SO_2 in the flue gas during each sampling test.

6.0   RESULTS AND DISCUSSION

As stated earlier, extensive SO_3 sampling tests were carried out by the EERC and MET at the R. Paul Smith Station. Results from the test are presented in this section. It is noted there was substantial air leakage across the plant (from the air heater inlet to the stack), resulting in dilution of the flue gas. This was indicated by the varying O_2 concentrations: 3.5% at the air heater inlet and 6.7% at the stack. Therefore, all the measured SO_3 gas-phase concentrations were corrected to a 3% O_2 level so that valid comparisons can be made.

6.1   Coal and Fly Ash Analyses

The coal fired at the R. Paul Smith Station was a low-sulfur Maryland eastern bituminous coal. Samples of the coal were taken and proximate–ultimate analysis completed. Also, XRF elemental analysis was done on the ashed coal and ESP hopper fly ash samples. The ESP fly ash samples were collected at the baseline condition (no SO_3 injection and no humidification). The coal and ash analysis results are shown in Tables 2 and 3.

As seen in Table 3, the alkali and alkaline-earth elements in the fly ash, including sodium, potassium, calcium, and magnesium, account for 5.01 wt% on a mass basis, which is typical for an eastern bituminous coal. This low alkali content is still much higher than the 0.2 wt% of total sulfur (in the form of SO_3) in ESP ash, indicating there is enough alkali and alkaline metals available in the fly ash to neutralize condensed SO_3. The same fly ash was also analyzed for sulfate content by ion chromatography. The results show around 85% of the total sulfur was in the form of sulfate in the fly ash.

Table 2. Analysis of the Coal Fired at the R. Paul Smith Station

Proximate Analysis, wt%	
Moisture Content	6.80
Volatile Matter	20.35
Fixed Carbon	64.5
Ash	15.15
Ultimate Analysis, wt%	
Hydrogen	3.92
Carbon	75.06
Nitrogen	1.50
Sulfur	0.79
Oxygen, by difference	3.58
Heating Value, Btu/lb	12,926
Coal Analysis	
Mercury, µg/g	0.366
Chlorides, µg/g	270

Table 3. XRF Analysis of the Coal and ESP Hopper Ash from the R. Paul Smith Station, wt% concentration as oxides

Constituent	Ashed Coal	ESP Hopper Ash (baseline)
SiO_2	53.3	47.9
Al_2O_3	29.9	25.8
Fe_2O_3	8.3	7.6
TiO_2	1.5	1.4
P_2O_5	0.5	0.5
CaO	1.3	1.3
MgO	1.4	0.4
Na_2O	0.4	0.4
K_2O	2.3	2.2
SO_3	1.1	0.2

6.2   Effect of the Air Heater on SO_3 Concentration Without Humidification

Following a baseline test (no SO_3 injection), tests were conducted with SO_3 injected approximately 30 feet (9.1 m) upstream of the air heater. For all tests, the vapor-phase SO_3 was sampled at the air heater inlet, the ESP inlet, and the stack simultaneously. The resulting vapor-phase SO_3 concentrations and the total removal efficiency are plotted in Figure 3 as a function of sampling location and different SO_3 injection levels. The injection level ranged from 0 (baseline operating condition) to 50 ppm. As shown in Table 2, the sulfur content of the coal was low resulting in an average measured vapor-phase SO_3 concentration at the air heater inlet location of only 2.28 ppmv for the baseline condition. This decreased to 0.12 ppmv at the stack. As the flue gas temperature decreased, the SO_3 was most likely scavenged from the flue gas gradually through diffusion and heterogeneous condensation of the SO_3 vapor. Once condensation occurred, the alkali material in the fly ash then neutralized the SO_3 aerosol.

When nominally 10 ppmv SO_3 gas was injected, the vapor-phase SO_3 concentration was about 12 ppmv at the air heater inlet and dropped to 4.12 ppmv at the ESP inlet and 2.8 ppmv at the stack. This trend in decreasing SO_3 concentration as a function of temperature (different sampling locations) was observed for all of the four SO_3 injection levels (0, 10, 30, and 50 ppmv).

In general, the temperature decreased from about 650°F (343°C) at the air heater inlet to 320°–350°F (160°–177°C) at the stack. As expected, the stack vapor-phase SO_3 concentrations increased as the SO_3 injection level increased. The stack vapor-phase SO_3 concentrations were 8.1 and 13.2 ppmv for the SO_3 injection levels of 30 and 50 ppm, respectively. As shown in Figure 3 and Table 4, the corresponding total SO_3 removal efficiencies between the air heater inlet location and the stack were >60% at all SO_3 concentrations. In general, the data showed an
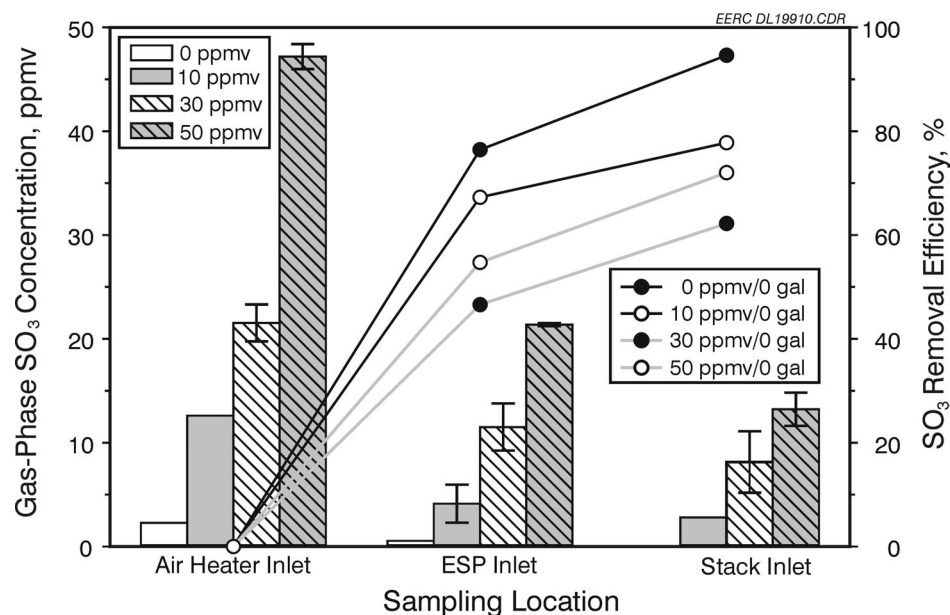
Figure 3. SO$_3$ concentration and removal efficiency with no humidification.

inverse correlation between the collection efficiency and initial SO$_3$ vapor concentration, which is in agreement with the theoretical analysis. However, when 50 ppm SO$_3$ was injected into the duct, the air heater removal efficiency was 72.2% compared to 62.2% at 30 ppmv. This may have been a result of changes in plant load that occurred between the different injection periods. As the plant load changes, the flow patterns through the air preheater also change, potentially resulting in cold spots that may cause SO$_3$ condensation.

Table 4. Vapor-Phase SO$_3$ Concentrations in Flue Gas as a Function of SO$_3$ Injection Levels, based on 3% O$_2$

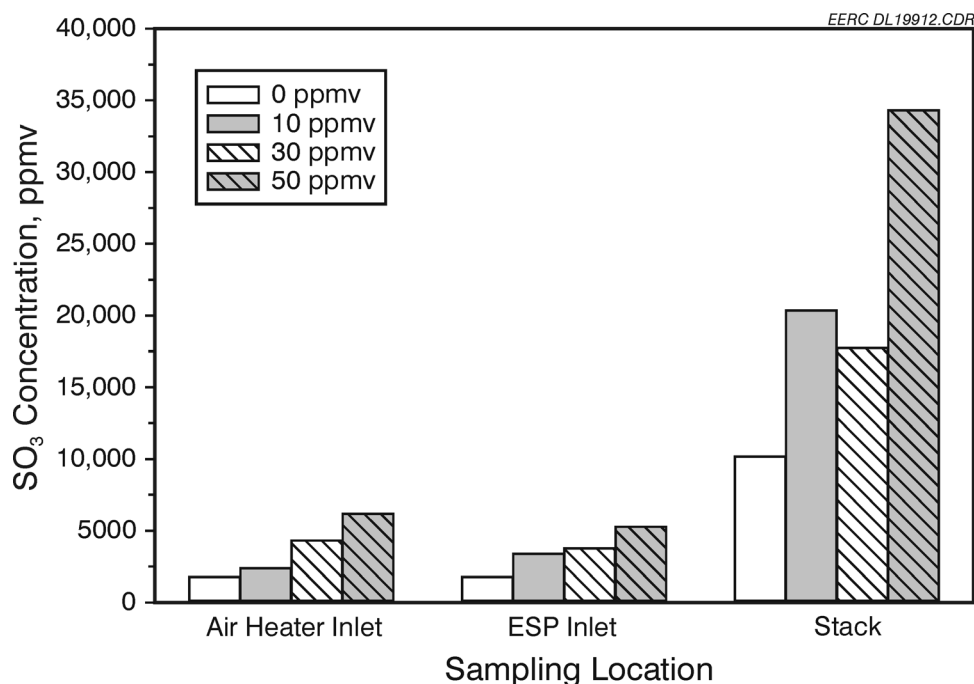| Nominal SO$_3$ Injection, ppmv	Sampling Location			Total Vapor-Phase SO$_3$ Removal, %
	Air Heater Inlet, ppmv	ESP Inlet, ppmv	Stack, ppmv	
0	2.28	0.54	0.12	94.6
10	12.6	4.12	2.80	77.8
30	21.5	11.5	8.13	62.2
50	47.2	21.4	13.2	72.2

Figure 4. SO$_3$ concentration in the fly ash with no humidification.

The fly ash samples collected from the EPA Method 5 filters at the three sampling locations were analyzed for sulfates (all sulfate concentrations were converted to SO$_3$ concentrations). The results are presented in Figure 4. With increasing SO$_3$ injection rates, from 0 to 50 ppmv, the sulfate concentration on the fly ash collected at the air heater increased from 1780 ppmv for the baseline condition up to 6180 ppmv when 50 ppmv was injected. These results indicate that the SO$_3$ vapor was transferred to the particulate phase during condensation. At the ESP inlet location, the sulfate concentrations of the fly ash ranged from 3381 to 5272 ppmv for the three injection tests (10, 30, and 50 ppmv). Therefore, there did not appear to be any further enrichment of sulfate on fly ash between the outlet of the air heater and ESP inlet (downstream of the humidification system). It appears that most of the depleted SO$_3$ vapor is condensed in the air heater. The sulfate was clearly enriched on the fine fly ash collected at the stack, as a result of condensation of SO$_3$ vapor on fly ash particles and the formation of sulfuric acid mist. The higher sulfate concentration on the fine fly ash at the stack when 50 ppmv SO$_3$ was injected, compared to the 10-ppmv injection test, indicated that more fine sulfate aerosols were formed in the ESP at the higher SO$_3$ concentration. Not surprisingly, the total sulfur concentrations in the fly ash were approximately the same as the sulfate concentration, showing most of the sulfur species were in the sulfate form.

As mentioned previously, the secondary particles generated by the SO$_3$ vapor are the main components determining the level of opacity at the stack of the power plant. On the other hand, based on the vapor- and solid-phase sampling results (plotted in Figures 3 and 4), SO$_3$ vapor was condensed as a sulfate and was collected by the ESP. Because of the high collection efficiency of fly ash in the ESP (usually higher than 99%), a high percentage of the converted SO$_3$ vapor is

then captured in the ESP. Therefore, by increasing the rate of SO_3 vapor condensation/reaction on the fly ash, prior to the ESP or fabric filter, SO_3 vapor emissions can be significantly reduced.

6.3   Effect of the Air Heater on SO_3 Concentration with Humidification

The humidification system was controlled to inject water into the duct prior to the ESP in a range of 0 to 12 gal/min (0–45.4 L/min). The effect of humidification on SO_3 is primarily through lowering the flue gas temperature. Because of mass-transfer limitations, very little direct collection of the SO_3 vapor happens by the water droplets. By lowering the flue gas temperature, SO_3 condensation is enhanced. Once the SO_3 has condensed on the fly ash particles, the ESP removes it from the flue gas. In addition, ESP performance is generally enhanced because of reduced flue gas temperature and presence of SO_3. Both of these factors reduce the ash resistivity, and a lower temperature results in a smaller flue gas volume. SO_3 samples were collected and analyzed at different humidification and SO_3 injection levels at the air heater inlet, ESP inlet, and the stack. Figure 5 and Table 5 show the results for the tests conducted at an SO_3 injection rate of 10 ppmv at three different levels of humidification (0, 8, and 12 gal/min [0, 30.3, 45.4 L/min]). The flue gas temperature at the stack averaged 344°F (173°C) without any humidification and was reduced to 306° and 274°F (152°–134°C) at the water injection rates of 8 and 12 gal/min (0, 30.3, and 45.4 L/min), respectively. The SO_3 gas concentration at the air heater inlet varied from 8 to 12 ppmv (nominal 10-ppmv SO_3 injection test), as a result of varying power plant operating conditions and fluctuation in the SO_3 injection system.
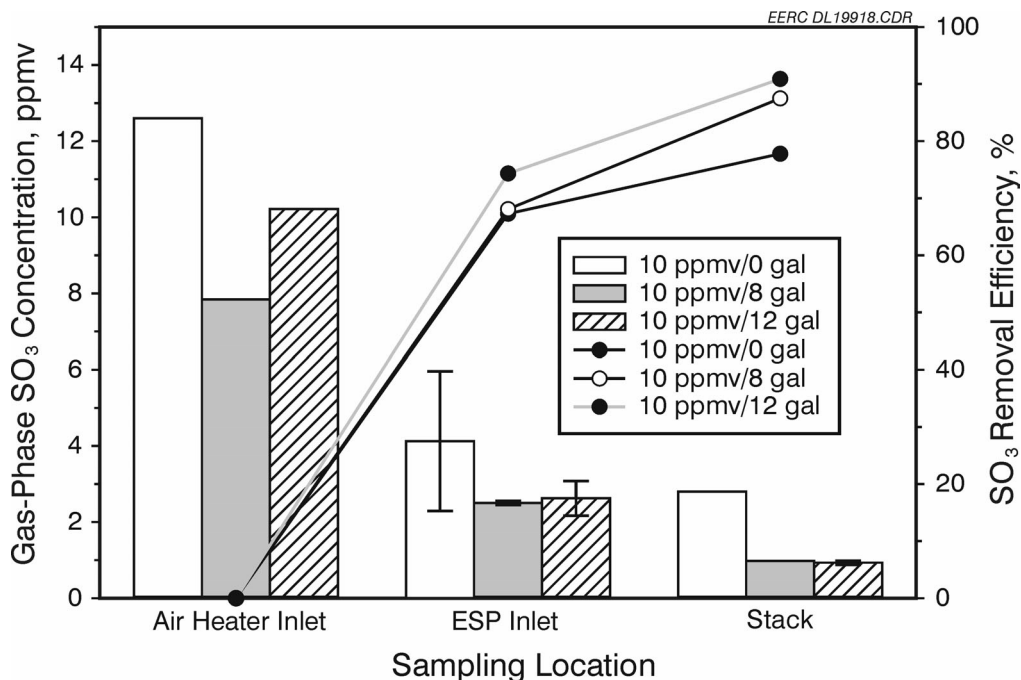

Figure 5. SO_3 concentration and removal efficiency as a function of humidification at a 10-ppmv SO_3 injection rate.

Table 5. SO$_3$ Concentrations for Three Flue Gas Humidification Levels and 10-ppmv SO$_3$ Injection Corrected to 3% O$_2$

Nominal Humidification gal/min	Stack Temp., °F	Air Heater Inlet, ppmv	ESP Inlet, ppmv	Stack Outlet, ppmv	Total Vapor-Phase SO$_3$ Removal,[a] %	Additional SO$_3$ Removal Due to Humidification[b] %
			Sampling Location			
0	344	12.6	4.12	2.80	77.7	0
8	286	7.84	2.50	0.98	87.5	17.8
12	274	10.22	2.62	0.93	90.9	18.3

[a] Calculated based on the air heater inlet SO$_3$ concentration compared to the stack SO$_3$ concentration.
[b] Calculated by subtracting the total SO$_3$ removed with no humidification from that calculated at the various humidification levels. To put all tests on the same basis, the average air heater inlet SO$_3$ concentration (10.2 ppmv) was used.

As shown in Table 5, the vapor-phase SO$_3$ concentration at the ESP inlet decreased from 4.12 ppmv without humidification to 2.5 and 2.6 ppmv as a result of humidification, resulting in an increase in total SO$_3$ vapor removal efficiency from 77.7% at no humidification to 87.5% and 90.9% at the humidification levels of 8 and 12 gal/min (30.3–45.4 L/min), respectively. Assuming a constant air heater inlet SO$_3$ concentration of 10.2 ppmv (average for all three tests), the effect of humidification is to increase the SO$_3$ removal efficiency by 15% to 20% when 10 ppmv SO$_3$ is injected in to the air heater inlet duct. It should be noted that the water injection system was only a few feet upstream of the ESP inlet sampling location; therefore, the enhanced SO$_3$ vapor removal is quite significant.

The stack concentration was below 1 ppmv with humidification (for all levels) compared to the 2.8 ppmv without humidification, clearly demonstrating that the use of humidification prior to the ESP reduces SO$_3$ vapor emission at the stack.

Figure 6 presents the sulfate concentrations (at 10 ppmv SO$_3$ injection) of the fly ash at each of the sampling locations and humidification levels. All results (sampling location and humidification levels) with humidification showed higher sulfate concentrations on the fly ash than those measured at the baseline condition. This would indicate that the SO$_3$ vapor was transferred to the particulate matter prior to the air heater. The sulfate concentrations on the fly ash collected at the air heater inlet and the ESP inlet were approximately the same, indicating no substantial sulfation occurring in the air heater. The data confirm that most of the gas-phase SO$_3$ reduction across the air heater was a result of condensation on the air heater surfaces. As before, with no humidification, the sulfate concentration on the very fine ash at the stack was significantly enriched.

The same type of humidification tests were then conducted at 30-ppmv and 50-ppmv SO$_3$ injection (see Tables 6 and 7). These tests were done at humidification rates of 0, 6, 9, and
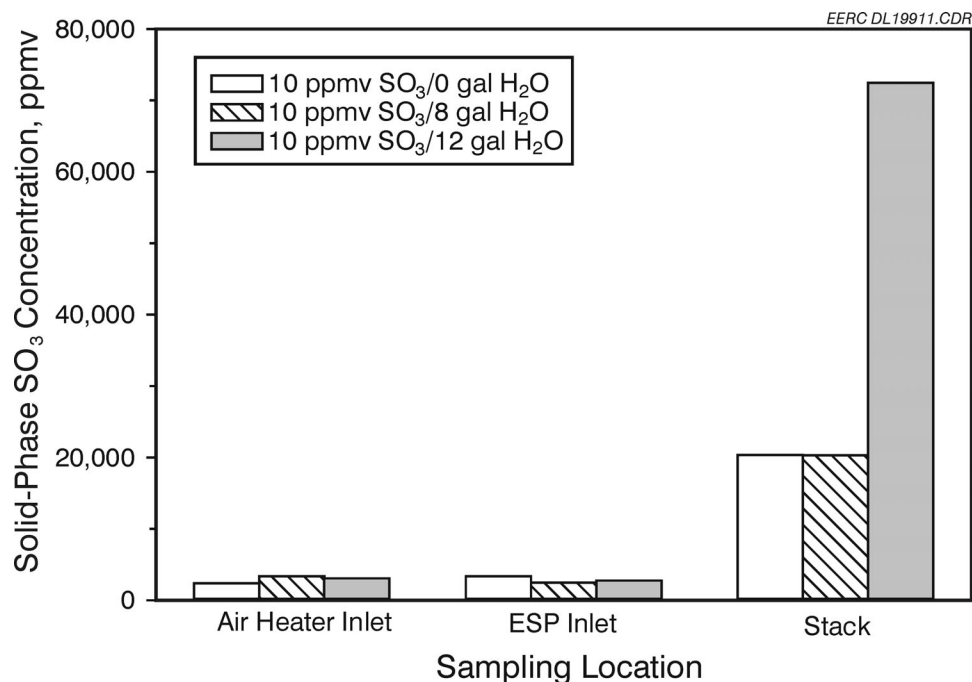
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Figure 6. SO$_3$ concentration in the fly ash as a function of humidification at a 10-ppmv SO$_3$ injection rate.

Table 6. SO$_3$ Concentrations for Three Flue Gas Humidification Levels and 30-ppmv SO$_3$ Injection Corrected to 3% O$_2$

Nominal Humidification, gal/min	Stack Temp., F	Sampling Location Air Heater Inlet, ppmv	ESP Inlet, ppmv	Stack, ppmv	Total Vapor-Phase SO$_3$ Removal,[a] %	Additional SO$_3$ Removal Because of Humidification,[b] %
0	320	21.5	11.5	8.13	62.2	0
6	309	27.7	9.32	7.92	71.4	0.7
9	289	35.1	7.11	4.12	88.3	14.0
12	274	29.9	7.00	2.27	92.4	20.5

[a] Calculated based on the air heater inlet SO$_3$ concentration compared to the stack SO$_3$ concentration.
[b] Calculated by subtracting the total SO$_3$ removed with no humidification from that calculated at the various humidification levels. To put all tests on the same basis, the average air heater inlet SO$_3$ concentration (28.6 ppmv) was used.

Table 7. SO$_3$ Concentrations for Three Flue Gas Humidification Levels and 50-ppmv SO$_3$ Injection Corrected to 3% O$_2$

		Sampling Location				
Nominal Humidification, gal/min	Stack Temp., °F	Air Heater Inlet, ppmv	ESP Inlet, ppmv	Stack, ppmv	Total Vapor-Phase SO$_3$ Removal,[a] %	Additional SO$_3$ Removal Due to Humidification,[b] %
0	315	47.2	21.4	13.2	72.0	0
6	295	45.5	17.5	9.76	78.8	7.6
9	285	29.4	15.7	7.17	75.6[c]	13.3
12	275	43.3	13.0	4.18	90.3	21.9

[a] Calculated based on the air heater inlet SO$_3$ concentration compared to the stack SO$_3$ concentration.
[b] Calculated by subtracting the total SO$_3$ removed with no humidification from that calculated at the various humidification levels. To put all tests on the same basis, the average air heater inlet SO$_3$ concentration (45.3 ppmv) was used (the air heater inlet value at 9 gal/min [34.07 L/min] is assumed to be a bad measurement and was ignored).
[c] If the average air heater inlet value of 45.3 ppmv is used, the total vapor-phase SO$_3$ removal is 84.2%.

12 gal/min (0, 22.7, 34.1, and 45.4 L/min). The results for these tests are also presented graphically in Figures 7 and 8. As shown in Figure 7, at an injection rate of 30 ppmv SO$_3$, without humidification, the fly ash could not remove the SO$_3$ efficiently, resulting in a relatively high SO$_3$ stack concentration of 8.1 ppm. Essentially the same results were obtained at a humidification level of 6 gal/min (22.7 L/min). This shows that at the higher SO$_3$ concentrations, greater levels of humidification are needed to reduce SO$_3$ emissions efficiently. At water injection rates of 9 and 12 gal/min (34.1 and 45.4 L/min), SO$_3$ vapor concentrations at the stack outlet were 4.1 and 2.3 ppmv, respectively. The corresponding SO$_3$ vapor collection efficiencies shown in Figure 7 demonstrate the effect of flue gas humidification more clearly. Figure 8 indicates that fly ash alone had an SO$_3$ vapor collection efficiency of 62.2% and only increased to 71.4% when the water injection rate was 6 gal/min (22.7 L/min). Considerably higher removal efficiencies were obtained at water injection rates of 9 and 12 gal/min (34.1 and 45.4 L/min), 88.2% and 92.4%, respectively. The improvement in SO$_3$ removal efficiency as a result of humidification is shown in Table 6.

At the 50-ppmv SO$_3$ injection rate, the SO$_3$ vapor concentrations across the system and the corresponding SO$_3$ vapor collection efficiencies are shown in Table 7 and Figure 9. For these tests, the SO$_3$ vapor injection was relatively constant, ranging from 43.3 to 47.2 ppmv; however, for the test with a humidification level of 9 gal/min (34.1 L/min), the SO$_3$ vapor at the air heater inlet was only 29.4 ppmv. Based on the data when 30 ppmv SO$_3$ was injected and a 9-gal/min (34.1-L/min) humidification rate is used, the overall SO$_3$ is significantly less, indicating the measurement was bad and the actual SO$_3$ concentration is more than likely higher.
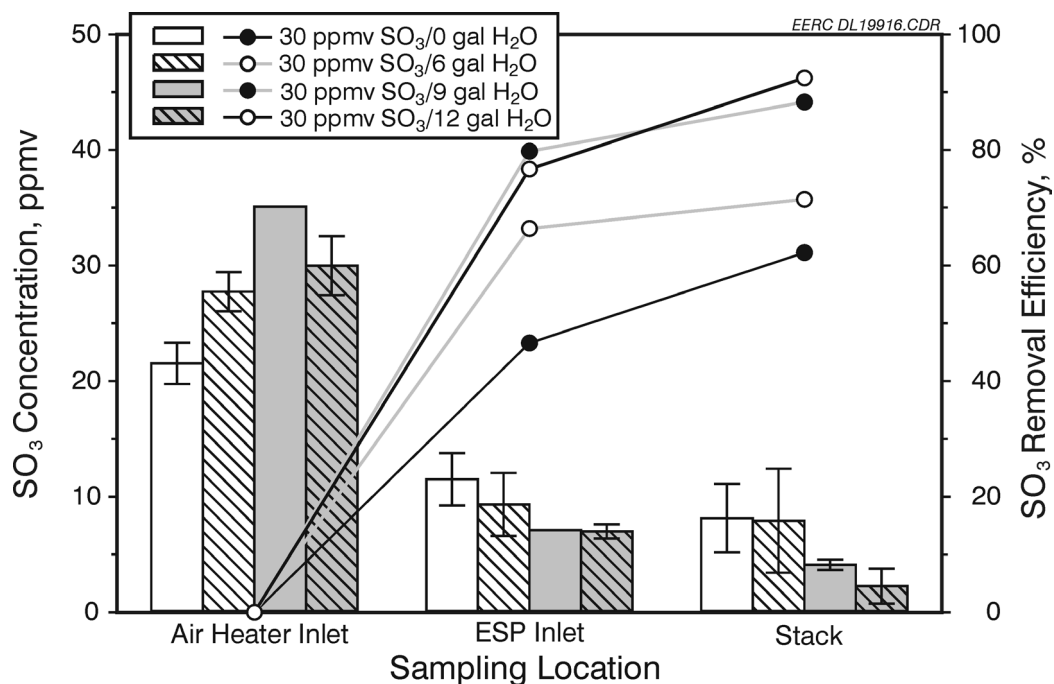
Figure 7. SO_3 concentration and removal efficiency as a function of humidification at a 30-ppmv SO_3 injection rate.
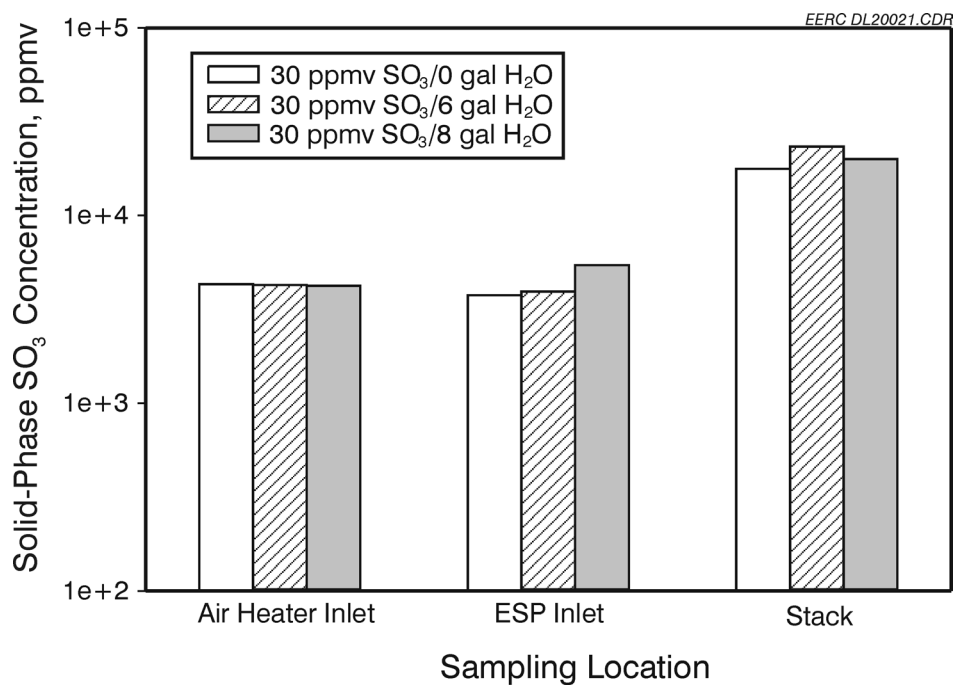

Figure 8. SO_3 concentration in the fly ash as a function of humidification at a 30-ppmv SO_3 injection rate.
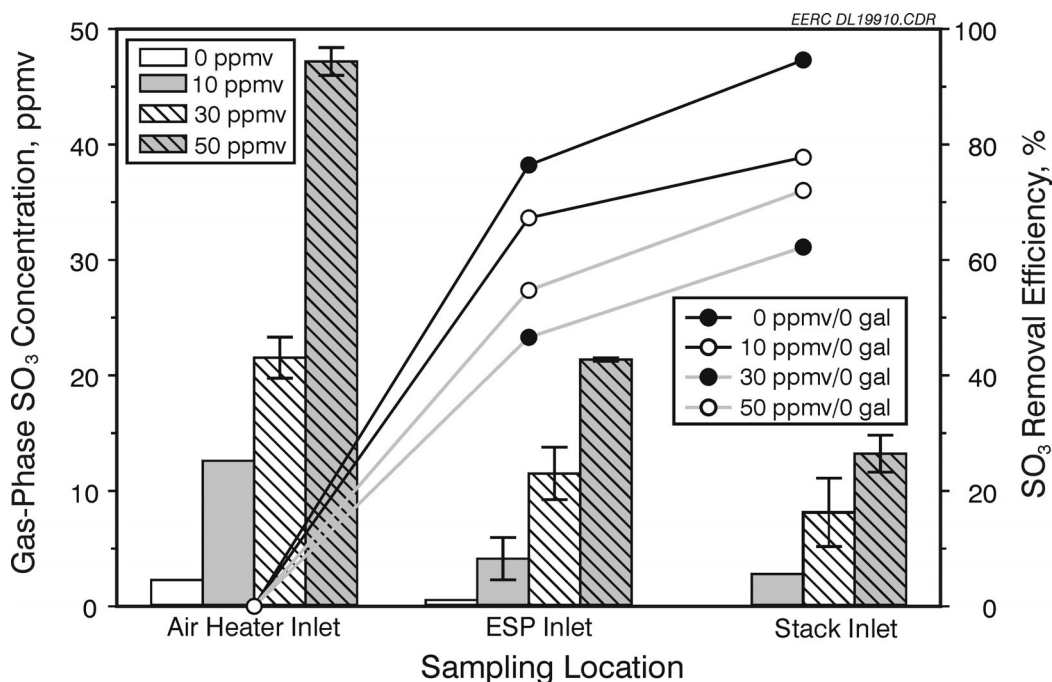
Figure 9. SO$_3$ concentration and removal efficiency as a function of humidification at a 50-ppmv SO$_3$ injection rate.

As in previous tests, the gas-phase SO$_3$ stack concentrations were significantly reduced with the increasing water injection rates. At a 12-gal/min (45.4-L/min) water injection rate, the measured SO$_3$ concentration was only 4.18 ppmv. The SO$_3$ vapor collection efficiencies were 72.0% with no water injection, 78.8% at a 6-gal/min (22.7-L/min) water injection rate, and 90.3% at a 12-gal/min (45.4-L/min) water injection rate. However, the SO$_3$ removal efficiency was only 75.6% for the test using a 9-gal/min (34.1-L/min) water injection rate. As explained earlier, it appears this may be a bad measurement.

The sulfate concentrations of the fly ash at the three sampling locations for the tests at SO$_3$ injection rates of 30 and 50 ppmv are plotted in Figures 8 and 10. Again, the data show no substantial increase of sulfate on fly ash between the air heater and the ESP inlet sampling location. Also, there was a substantial enrichment of sulfate observed on the fine particles at the stack for all of the tests, although enrichment was greater as a result of 50-ppmv SO$_3$ injection.

6.3.1 Effect of Temperature on SO$_3$ Removal

As discussed above, by injecting water into the flue gas to reduce the temperature, the condensation of SO$_3$ vapor on fly ash was enhanced. Combining the improved ESP performance due to reduced fly ash resistivity (higher sulfate concentration on fly ash) and the lower flue gas temperature, the overall SO$_3$ collection efficiency was substantially increased with flue gas humidification. The SO$_3$ collection efficiencies for the SO$_3$ injection tests are plotted as a function of flue gas temperature at the stack in Figure 11. It should be noted that variation in coal and plant operation result not only in changes in flue gas temperature but also in fly ash
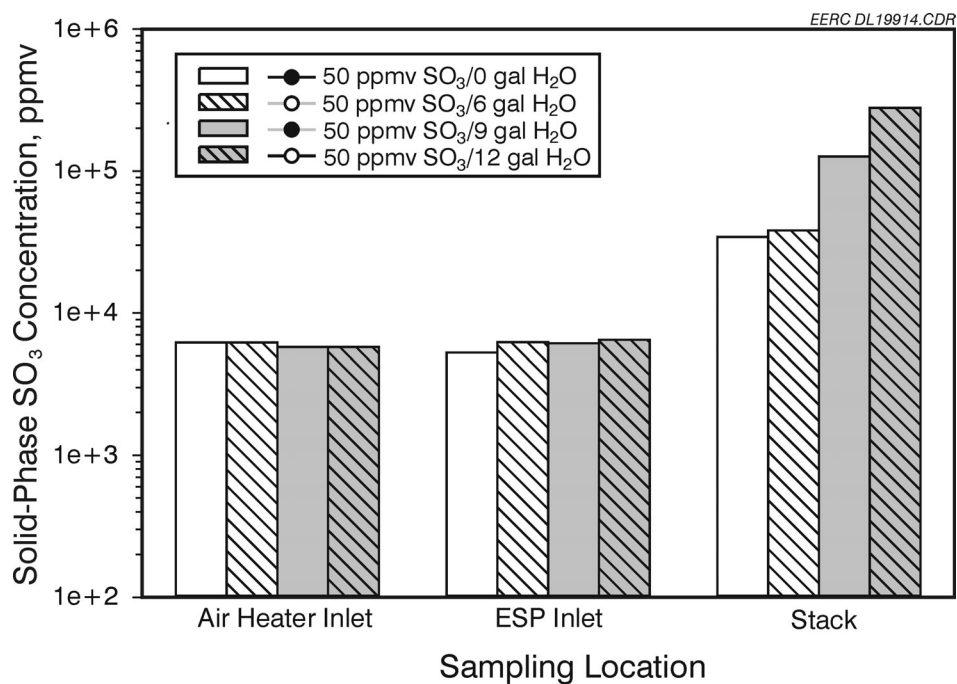
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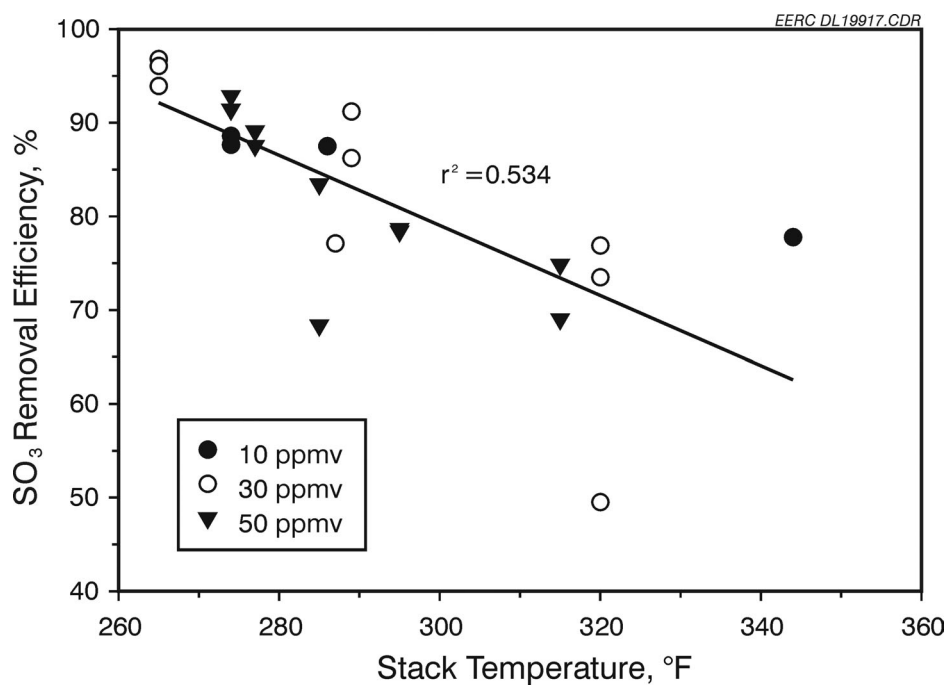Figure 10. SO$_3$ concentration in the fly ash as a function of humidification at a 50-ppmv SO$_3$ injection rate.

Figure 11. Overall SO$_3$ removal efficiency as a function of stack temperature.

16

properties dust loading. These changes, in turn affect the SO_3 vapor condensation across the system. Thereafter, the SO_3 removal efficiency also varied, even at the same stack temperature. However, given these variations and those in the SO_3 injection rates, the results appear to be relatively linear, as shown by the regression line in Figure 11. The flue gas temperature at the stack varied from 265° to 344°F (129° to 173°C), depending on the water injection rate. The lower flue gas temperature obtained at the higher water injection rate consistently resulted in improved SO_3 collection efficiency, regardless of SO_3 flue gas concentration. The SO_3 collection efficiency was the highest, >92%, at the lowest flue gas temperature.

6.3.2 Mercury

Although mercury was not the focus of the tests at the R. Paul Smith Station, OH mercury speciation measurements were made during several of the tests. The results are shown in Figure 12. The mercury generated by the coal was high: about 42 $\mu g/Nm^3$ in the flue gas. This is consistent with the mercury content measured in the coal of 0.366 $\mu g/g$ (presented in Table 2). The average coal mercury data based on the EPA Information Collection Request (found at http://www.epa.gov/ttnatw/combust/utiltox/utoxpg.html) was 0.11 $\mu g/g$. However, as shown in Figure 12, a high percentage of the mercury, approximately 75%, is associated with the particulate matter. This portion of the mercury is removed by the ESP, resulting in overall mercury concentrations of about 7 $\mu g/Nm^3$ at the stack.

It appears that the addition of SO_3 increased mercury emissions by converting some of the particulate-bound mercury to oxidized mercury. However, the results are based on only a few
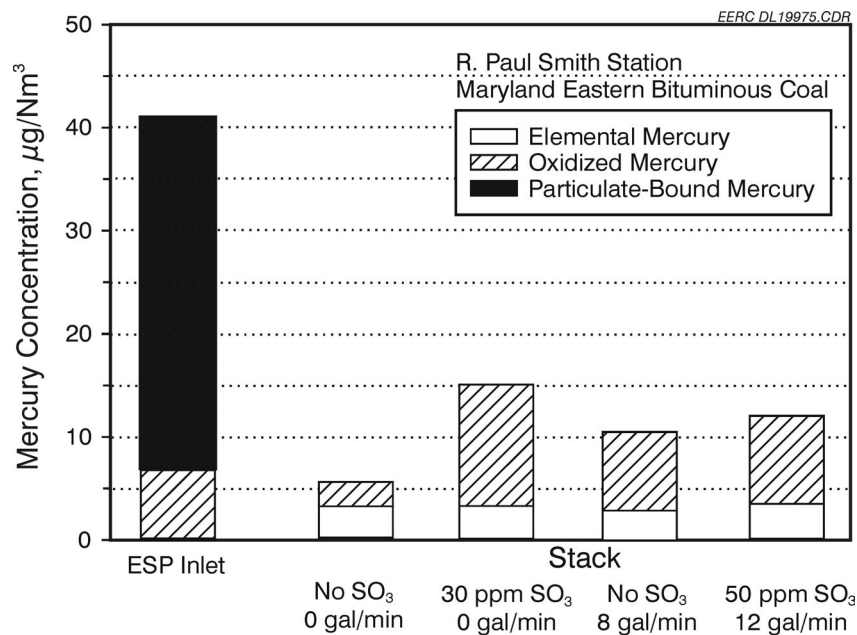

Figure 12. Flue gas mercury concentration at the R. Paul Smith Station as a function of SO_3 injection and humidification.

data points. A much more extensive study would be necessary to determine the impact of SO_3 and/or humidification on mercury speciation and mercury emissions.

7.0   CONCLUSIONS AND RECOMMENDATIONS

The conclusions resulting from the sampling at the R. Paul Smith Station to determine the effect of humidification on SO_3 emissions are as follows:

- The air heater was able to remove SO_3 efficiently, 94.6%, at the baseline condition (no SO_3 injection or humidification).

- Higher SO_3 concentrations up to 13 ppmv were measured at the stack when 50 ppm SO_3 was injected into the flue gas upstream of the air heater.

- SO_3 concentrations were significantly reduced with flue gas humidification: the higher the water injection rate, the lower the SO_3 concentration at the stack. For example, at 12 gal/min (45.4 L/min) of water, SO_3 concentration at the stack was only 4 ppmv when 50 ppm SO_3 was injected into the flue gas.

- The highest SO_3 collection efficiency at the stack, 96.8%, was achieved at a flue gas temperature of 265°F (129°C).

- Overall, the data demonstrated a strong potential to reduce SO_3 emissions using flue gas humidification.

- It is important to keep in mind that material corrosion might be a problem; therefore, it is suggested that flue gas temperature not be lower than 230°F (110°C).

- Reducing water droplet size, resulting in faster vaporization in the flue gas, would result in improvements to the humidification system.

8.0   REFERENCES

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